“Chemical Synthesis and Electrochemical Properties of Doped Metal Organic Frameworks”

Synopsis in Candidature for the Degree of

Doctor of Philosophy in chemistry

Submitted by

Mr. Yahya Nasser Saleh Abu Fatma

Under the guidance of

Dr. G. Krishna Chaitanya

School of Chemical Science

Submitted to

Swami Ramanand Teerth Marathawada University, Nanded

2025-2026.

1. Introduction

Metal-organic frameworks (MOFs) have emerged as a promising class of materials for various applications, including energy storage, catalysis, and sensing, due to their high surface area, varying structure, and diverse functionality. Doped MOFs with heteroatoms or metal ions can significantly enhance their electrochemical properties, making them suitable for advanced applications like batteries and fuel cells. The global transition toward sustainable energy technologies has intensified the search for advanced functional materials with tailored properties. MOFs have emerged as a premier class of porous crystalline materials, constructed from metal ions or clusters interconnected by organic binders [1]. Their characteristics like exceptional surface area, ultrahigh porosity, and structural engineering have propelled their exploration beyond traditional applications in gas storage and separation into the frontier of electrochemical energy systems [2]. In electrochemical properties context, such as supercapacitors, batteries, and electrocatalysts, MOFs offer unique advantages. Their ordered porous structures can facilitate rapid ion transport, while their synthetic flexibility allows for the precise placement of redox-active sites [3]. However, the practical deployment of many pristine MOFs in these roles is often constrained by intrinsic limitations, most notably poor electronic conductivity and moderate stability under operational electrochemical conditions [4]. To overcome these barriers and unlock the full electrochemical potential of MOFs, chemical doping has emerged as a powerful and versatile strategy. Doping involves the intentional introduction of heteroatoms, foreign metal ions, or functional groups into the MOF's architecture, either at the metal nodes, within the organic binders, or in their pores [5]. This process can profoundly alter the material's electronic structure, enhance conductivity, introduce new catalytic sites, and improve chemical stability without drastically compromising its inherent porosity [6]. The specific methodology of doping *via* direct

(one-pot) synthesis, post-synthetic modification, or thermal treatment serves as a critical determinant of the resulting material's properties. Each approach offers distinct advantages in terms of doping uniformity, site specificity, and framework integrity [7]. Consequently, establishing clear synthesis-property relationships is paramount. A systematic investigation that correlates specific doping strategies (type of dopant, method of incorporation, concentration) with measurable electrochemical outputs (capacitance, catalytic activity, conductivity, cycling stability) is essential for the rational design of high-performance materials [8]. The project will focus on the rational chemical synthesis, comprehensive characterization, and detailed electrochemical evaluation of a series of doped MOFs. Primary objectives include: a) developing optimized synthetic protocols for incorporating selected dopants (e.g., heteroatoms like N or S, or transition metals like Co, Ni, Fe) into model MOF platforms; b) characterizing the structural, morphological, and compositional consequences of doping using advanced analytical techniques; and b) rigorously evaluating the electrochemical performance of the doped materials in relevant applications, such as supercapacitive energy storage and electrocatalytic oxygen evolution. By methodically linking synthetic parameters to functional performance, it is planned to contribute fundamental insights and establish design principles for the next generation of electrochemically active doped MOF-based materials.

2. Literature review

Lokhande et al. reviewed MOF-derived nano/micro hybrid materials as advanced electrode materials for supercapacitors, highlighting their structural tunability, high porosity, and enhanced electrochemical performance [9, 10]. *Muratov et al.* synthesized Mn-doped MOF *via* partial substitution of cobalt using an ultrasonication-assisted aqueous method. After controlled pyrolysis,

the doped MOF-derived electrodes revealed enhanced electrochemical performance, with specific capacitance increasing from ~100 to 298 F g^{-1} at 0.25 A g^{-1}. The study confirmed that metal doping effectively improves the electrochemical properties of MOFs for energy storage applications[10]. *Yang et al.* synthesized a layered Ni-based metal–organic framework and applied as a supercapacitor electrode material. The Ni-based MOF exhibited high specific capacitance, excellent rate capability, and good cycling stability, achieving 1127 and 668 F g^{-1} at 0.5 and 10 A g^{-1}, respectively, with over 90% capacitance retention after 3000 cycles [11]. *Nagaraju et al.* fabricated MOF-derived hollow $Cu(Co–Ni)_2S_4$ nanotubes as a binder-free electrode, showing high areal and specific capacities and good cycling stability. The assembled hybrid supercapacitor delivered high energy and power densities with excellent efficiency, confirming its potential for advanced energy storage applications[12]. *Kalyon et al.* synthesized Cu- and Zn-based MOFs and, for the first time, incorporated them as additives into polypyrrole electrodes *via* in-situ electrochemical polymerization for supercapacitor applications. The optimized MOF/PPy composite electrodes exhibited enhanced electrochemical performance, achieving areal capacitances of 234.4 and 127.1 mF cm^{-2} at 1 mA cm^{-2} for Zn- and Cu-based MOFs, respectively[13].

3. Synthesis Method

In hydrothermal synthesis method there is the synthesis of electrode materials in various nanostructures on conducting and non-conducting substrate surfaces at temperature of less than 200 ^oC and ambient pressure. In this process, there is the teflon-lined stainless-steel autoclave which possess the base current collector in the presence of suitable solvent at an annealing temperature less than 200 ^oC for 1-10 h. There is the production of the MOF material due to

reaction bath pressure and temperature. Therefore, this chemical synthesis of MOF facilitates phase pure formation of the MOF, direct doping can change physical and chemical properties of host MOF, excess active sites, higher surface area etc. [14, 15].

4. Physical and Electrochemical Measurements

X-ray diffraction (XRD) is a powerful technique used to analyze the crystal structure, phase purity, and crystallite size of electrode materials. This spectroscopic technique is used to identify the atomic and molecular structure of crystal. it also used to differentiate the nature of crystalline materials from nanocrystalline materials and the structure identification is made from the x-ray diffraction pattern analysis. When X-rays interact with the atoms in a crystal, they produce a diffraction pattern that provides information about the atomic arrangement. Field-emission scanning electron microscopy (FESEM) is a tool for investigation of the surface morphology and posture of the sample material. It gives detailed images of the surface morphology and microstructure of electrode materials. [16]. X-ray Photoelectron Spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that provides detailed information about the surface elemental composition and chemical states of elements present within a few nanometers of the material's surface. In summary XPS measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. Thus, it helps correlate surface chemistry with charge storage mechanisms and stability. Raman spectroscopy provides information on vibrational modes, structural ordering of materials and material defects. It is sensitive to lattice distortions and bonding environments. Raman spectroscopy uses scattering of laser light to probe molecular structure. Of every million photons scattered, a single photon will interact with the vibrational states of a sample molecule and emit light of a different wavelength. also Raman systems can be configured to explore molecular structure as effectively as IR

spectroscopy. Fourier Transform Infrared Spectroscopy (FTIR) identifies functional groups and chemical bonds in the nanostructures by measuring the absorption of infrared radiation at different wavelengths. FTIR confirms the formation of Bi–O, Sb-O, and metal-halide bonds. These functional groups can enhance ion transport, wettability, and faradaic redox reactions. Brunauer–Emmett–Teller (BET) Analysis measures the specific surface area and pore size distribution by nitrogen adsorption–desorption isotherms. It is essential for correlating surface properties with electrochemical performance. BET data helps to obtain information on micro-, meso-, and macroporosities of electrode materials. Cyclic Voltammetry (CV) as an important electrochemical technique in supercapacitor which measures the current that develops in an electrochemical cell. As well as is a powerful tool to study redox behavior, capacitance, and electrochemical reversibility. CV scans will also be used to determine the electron stoichiometry of a system, the diffusion coefficient of an analyte and the formal reduction potential[17]. Galvanostatic Charge-Discharge (GCD) provides direct measurement of charge storage efficiency. The charge-discharge curves offer all information about electrode material including specific capacitance, stability, power and energy densities etc. The current density remains constant in charge- discharge curve with constant potential window to evaluate performance stability and it can be changed for obtaining different values of the discharge time between the two potentials. In charge process the curve may begin from zero time or any value in the range of potential window and it increases linearly up to the desired potential. Then, it reveres its direction to come back to the original value within a certain time [18]. Electrochemical Impedance Spectroscopy (EIS) measures the impedance of a system in dependence of the AC potentials frequency. Frequency-dependent impedance analysis provides insight into ion diffusion and conductivity. This technique measures resistance components, including solution resistance, charge transfer resistance, and double-layer

capacitance. As well as is a powerful nondestructive tool to study chemical and physical processes in solutions as well as in solids [19].

5. Objectives and topic of research undertaken

Doped MOF nanostructures introduce novel avenues for the advancement of clean and sustainable energy technologies, encompassing efficient energy storage solutions. It is believed that the doped MOFs can demonstrate ameliorated physical and chemical properties for obtaining elevated electrochemical energy storage performance. Furthermore, the incorporation foreign materials in to MOF nanostructures may further refine their functional attributes, leading to the development of more efficient, stable, and adaptable electrode materials for energy storage devices.

This study is designed to achieve the following objectives:

a) Synthesis and physical and chemical characterizations of the MOFs-based nanostructures either by chemical or green chemical process.

b) Efforts will be made to dope the as-obtained MOF electrode materials with either metal oxide, polymer, or chalcogenides, halides, or mixed forms using the ion exchange method.

c) It is planned to investigate the influence of dopant on the structure, surface area and morphology on the electrochemical and electrocatalysis properties of the MOF nanostructured electrodes.

d) Various electrochemical parameters, like power density, energy density, specific capacitance etc., will be obtained for both undoed and undoped MOF nanostructured electrodes.

e) Efforts will be also made to understand experimental results theoretically.

f) The best performing doped-MOF nanostructured electrodes will be employed in making energy storage devices for laboratory scale electronic applications.

g) Based on experimental results and theoretical understanding, results will be summarized and conclusions will be made for knowing suitability of the as-synthesized pristine and doped MOF in electrochemical supercapacitor technologies.

h) Manuscripts will be written, and published in highly reputed/indexed journals.

References

[1] H. Furukawa, K. E. Cordova, M. O'Keeffe, and O. M. Yaghi, "The chemistry and applications of metal-organic frameworks," *Science (80-.).*, vol. 341, no. 6149, p. 1230444, 2013.

[2] H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, "Design and synthesis of an exceptionally stable and highly porous metal-organic framework," *Nature*, vol. 402, no. 6759, pp. 276–279, 1999.

[3] D. Sheberla, J. C. Bachman, J. S. Elias, C.-J. Sun, Y. Shao-Horn, and M. Dinc\ua, "Conductive MOF electrodes for stable supercapacitors with high areal capacitance," *Nat. Mater.*, vol. 16, no. 2, pp. 220–224, 2017.

[4] S. Zhou, T. Liu, M. Strømme, and C. Xu, "Electrochemical Doping and Structural Modulation of Conductive Metal-Organic Frameworks," *Angew. Chemie Int. Ed.*, vol. 63, no. 14, p. e202318387, 2024.

[5] C. Pettinari and A. Tombesi, "MOFs for electrochemical energy conversion and storage,"

Inorganics, vol. 11, no. 2, p. 65, 2023.

[6] Y. Tang, H. Zhang, Y. Jin, J. Shi, and R. Zou, “Boosting the electrochemical energy storage and conversion performance by structural distortion in metal--organic frameworks,” *Chem. Eng. J.*, vol. 443, p. 136269, 2022.

[7] H. Bin Wu and X. W. Lou, “Metal-organic frameworks and their derived materials for electrochemical energy storage and conversion: Promises and challenges,” *Sci. Adv.*, vol. 3, no. 12, p. eaap9252, 2017.

[8] X. F. Lu, Y. Fang, D. Luan, and X. W. D. Lou, “Metal--organic frameworks derived functional materials for electrochemical energy storage and conversion: a mini review,” *Nano Lett.*, vol. 21, no. 4, pp. 1555–1565, 2021.

[9] P. E. Lokhande *et al.*, “The progress and roadmap of metal--organic frameworks for high-performance supercapacitors,” *Coord. Chem. Rev.*, vol. 473, p. 214771, 2022.

[10] D. G. Muratov, L. V Kozhitov, I. V Zaporotskova, A. V Popkova, V. V Sleptsov, and A. V Zorin, “Metal-organic frameworks and composites on their basis: structure, synthesis methods, electrochemical properties and application prospects (a review),” *Mod. Electron. Mater.*, vol. 10, no. 2, pp. 61–84, 2024.

[11] J. Yang, P. Xiong, C. Zheng, H. Qiu, and M. Wei, “Metal--organic frameworks: a new promising class of materials for a high performance supercapacitor electrode,” *J. Mater. Chem. A*, vol. 2, no. 39, pp. 16640–16644, 2014.

[12] G. Nagaraju, S. C. Sekhar, B. Ramulu, and J. S. Yu, “High-performance hybrid

supercapacitors based on MOF-derived hollow ternary chalcogenides," *Energy Storage Mater.*, vol. 35, pp. 750–760, 2021.

[13] H. Y. Kalyon, M. Gencten, S. Gorduk, and Y. Sahin, "Novel composite materials consisting of polypyrrole and metal organic frameworks for supercapacitor applications," *J. Energy Storage*, vol. 48, p. 103699, 2022.

[14] T. M. Al-Hejri *et al.*, "Electrochemical Supercapacitor and Water Splitting Electrocatalysis Applications of Self-Grown Amorphous Ni (OH) 2 Nanosponge-balls," *Electrochim. Acta*, p. 143516, 2023.

[15] T. M. Al-Hejri, H. M. Danamah, V. V Jadhav, S. F. Shaikh, and R. S. Mane, "Bi2O3@TiO2 p-n hetero-junction electrode: A promising approach for improving energy storage performance," *J. Energy Storage*, vol. 115, p. 115996, 2025, doi: https://doi.org/10.1016/j.est.2025.115996.

[16] T. M. Al-Hejri, V. V Jadhav, H. M. Danamah, T. Siddiqui, S. F. Shaikh, and R. S. Mane, "Exploring Ni(OH)2@Bi2O3 p-p Hetero-junction electrode for enhanced energy storage performance," *J. Power Sources*, vol. 644, p. 237026, 2025, doi: https://doi.org/10.1016/j.jpowsour.2025.237026.

[17] H. M. Danamah, V. V Jadhav, T. M. Al-Hejri, S. F. Shaikh, A. M. Al-Enizi, and R. S. Mane, "Surface morphology-tailored electrochemical supercapacitor and better hydrogen evolution reaction activities of Bi2S3 nanostructures," *J. Energy Storage*, vol. 97, p. 112323, 2024, doi: https://doi.org/10.1016/j.est.2024.112323.

[18] H. M. Danamah, Z. A. Shaikh, T. M. Al-Hejri, T. A. J. Siddiqui, V. V. Jadhav, and R. S.

Mane, “Conversion of the Bi2O3 to Bi2S3: An ion exchange strategy for tailoring the surface morphology with accrued energy storage performance,” *J. Energy Storage*, vol. 78, no. October 2023, p. 109820, 2024, doi: 10.1016/j.est.2023.109820.

[19] H. M. Danamah, V. V Jadhav, T. M. Al-hejri, F. Shaikh, A. M. Al-enizi, and R. S. Mane, “Surface morphology-tailored electrochemical supercapacitor and better hydrogen evolution reaction activities of Bi 2 S 3 nanostructures,” *J. Energy Storage*, vol. 97, no. PA, p. 112323, 2024, doi: 10.1016/j.est.2024.112323.

[20] T. M. Al-Hejri *et al.*, “Facile fabrication of the Ni(OH)2–Bi2O3@NiF p-p hetero-junction electrocatalyst for efficient water splitting application,” *Int. J. Hydrogen Energy*, vol. 124, pp. 290–303, 2025, doi: https://doi.org/10.1016/j.ijhydene.2025.03.392.

[21] A. H. Al-Naggar *et al.*, “Self-supported iron-doped nickel oxide multifunctional electrodes for highly efficient energy storage and overall water-splitting uses,” *J. Energy Storage*, vol. 86, p. 111363, 2024, doi: https://doi.org/10.1016/j.est.2024.111363.

Research scholar

Yahya Nasser Saleh Abu Fatma

Research Guide

prof. G. Krishna Chaitanya

School of Chemical science

S.R.T.M.U. Nanded